

Report for 2002MD3B: Atmospheric Deposition of Currently Used Pesticides to Chesapeake Bay Watersheds.

- Articles in Refereed Scientific Journals:
 - Kuang, Z., McConnell, L. L., Torrents, A., Merritt, D., Tobash, S. (2003) Atmospheric deposition of currently used pesticides to the Choptank River watershed J. of Environmental Quality (in press).

Report Follows:

Annual Report for the period 3/01/02 through 2/28/03

Project Title: Atmospheric Deposition of Currently Used Pesticides Chesapeake Bay Watersheds

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Problem and Research Objectives

The Delmarva Peninsula, a region within the Chesapeake Bay watershed, is dominated by agricultural land use, which makes the streams and tributaries in this area highly vulnerable to agricultural runoff. This area also contains some of the most important aquatic habitat areas for the living resources of the Bay. The extent of local or regional atmospheric transport and deposition of pesticides to this area is poorly understood and may be an important contributor to the overall pesticide budget for the region. Baseline measurements of atmospheric concentrations and deposition fluxes of pesticides in different parts of the Chesapeake Bay watershed are a fundamental part of determining the importance of atmospheric processes to the overall loading of pesticides to the Bay.

As part of the Maryland's Targeted Watershed Project a number of government organizations and environmental groups are monitoring these watersheds in order to quantify the impacts of land use and non-point pollution control practices on water quality and aquatic life habitat and to determine long-term trends in water quality and aquatic life communities. While the potential for runoff of pesticides as a source of non-point pollution into surface waters is high, atmospheric deposition of pesticides that have been volatilized from local and regional agricultural activity may also play a significant role in water quality deterioration. The Delmarva Peninsula is poorly characterized with respect to the presence of pesticides in its atmosphere. This has hindered our ability to assess the importance of atmospheric loadings to the concentrations of these compounds in the Chesapeake Bay.

The general objective of this research is to characterize the Delmarva Peninsula with respect to the presence of pesticides in its atmosphere with a view to estimating aerial pesticide loadings to the Bay arising from agricultural activity in the Peninsula. In the previous report we presented in detail the sampling and analytical methodology. While sampling and analytical analysis has continued during this reporting period, during this reporting period we have increased our efforts on data analysis with respect to temporal trends in aerial concentrations/atmospheric depositions.

Methodology

As stated, the methodology was mostly developed during the previous reporting period and it has now been accepted for publication (Kuang et al. 2003).

Assessing temporal/spatial trends in the aerial concentration of pesticides

The pesticides being analyzed for in the samples from the Peninsula include those that have been banned and those that are currently being used in the region. In the air samples from 2000, chlorothalonil, metolachlor and a-endosulfan were above the limit of quantification in all samples (n = 31). Atrazine, HCHs, chlordanes, chlorpyrifos and b-endosulfan also occurred frequently (>80%). Chlorothalonil is the most frequently detected pesticide in rainfall. Atrazine degradation products, CIAT and CEAT seen in rainfall, were below the level of quantification in air samples.

In the past few decades awareness about the harmful ecological effects of organochlorine pesticides has led to their limited use or completely phase out. DDTs, chlordanes, HCHs are some pesticides in question. DDT is no longer registered for use in the U.S. Owing to concerns about the risk of cancer; the use of chlordane was banned by the USEPA in 1988. The insecticide is no longer distributed in the U.S. Similarly, Lindane (g-HCH) is no longer manufactured in the U.S. and hence its use is severely restricted (it is still being used in small amounts in the Delmarva). Heptachlor is another pesticide the use of which has been cancelled in the U.S. since 1988. It follows that since these pesticides are no longer being used in agriculture in this country, their concentrations in the environmental compartments should go down with time. For the pesticides currently being used, the concentrations in the atmosphere should be a function of usage, time and temperature.

Chlordanes are present in quantifiable amounts in the air in the Delmarva Peninsula although the concentrations are usually below the limit of quantification in rainfall (data not shown) and water bodies (Choptank river). DDT and its metabolites (DDEs) are below the level of quantification in both air and rainfall. Dieldrin has been sporadically detected in rainfall, which suggests that it might be present in quantifiable amounts in air. Heptachlor and its metabolite were sporadically seen in very small concentrations in precipitation at Horn Point.

Pesticides in precipitation over the Peninsula

Chlorothalonil is by far the most abundant pesticide in precipitation, forming 35-46% of the total flux (Table. 1). Atrazine and metolachlor are the second and third most abundant compounds. There appears to be a decrease in the wet deposition of herbicides atrazine and the fungicide chlorothalonil while the deposition of trifluralin and chlorpyrifos seems to be on the rise. Also the overall deposition of the pesticides seems to be on the decline. These observations suggest that the pesticide usage patterns in the region are changing and the changes are being reflected in the concentrations in precipitation. As more data for the 2002-2003 season becomes available, we will compare the rainfall fluxes data with the usage of pesticides over the years to ascertain if indeed the changes in fluxes are caused by changes in usage patterns. The spatial trends in wet fluxes for the Upper Delmarva Peninsula shall be examined by comparing the trends from the two sites two sites on the opposite ends of the Peninsula (Horn Point and Lewes).

Table 1. Pesticides in rainfall (Horn Point)

Yearly flux (total ng.m ⁻² /total rainfall)			
	2000	2001	2002
Volume, mL	128714	95637	156267
Rainfall (cm)	64	48	78
trifluralin	0.0	0.8	2.3
diazinon	1.7	1.9	27.7
g-HCH	4.1	5.6	2.6
chlorothalonil	627.5	430.3	252.0
chlorpyrifos	4.7	7.0	14.0
malathion	7.3	0.7	0.5
chlpyrfs oxon	22.6	38.8	23.3
a-endosulfan	4.1	5.7	1.1
b-endosulfan	11.5	7.9	1.9
endslfn slft	2.1	2.8	3.0
Atrazine	3.1	2.4	1.8
metolachlor	3.1	2.4	2.4
Total flux	2735	2173	1447

Effect of temperature on ambient concentrations: The Clausius Clapeyron Equation

In the case of atmospheric measurements of semivolatile compounds, the largest source of variability is related to atmospheric temperature (Cortes et al., 1998; Hillery et al., 1997). At elevated temperatures, the air concentrations increase indicating that volatilization from the earth's surface is an important factor in the movement of these chemicals. The effect on temperature on ambient concentrations of PCBs and PAHs is well documented (Simcik et al., 1999; Sofuoglu et al., 2001). Sofuoglu et al. (2001) also found statistically significant temperature dependence for gas phase DDD and trans-nonachlor in Chicago air.

Gas phase partial pressures increase as temperature increases and the functional relationship between these two parameters is given by the Clausius-Clapeyron (CC) equation:

$$\ln P = -\Delta H/RT + \text{constant}$$

Where P is the partial pressure of the compound (atm), ΔH is the characteristic phase-transition energy of the compound (kJ/mol), R is the gas constant and T is the temperature (K). Partial pressures can be obtained from atmospheric concentrations using the ideal gas law. Thus the plot of the natural logarithm of the partial vapor pressure as a

function of the inverse temperature will be a straight line. Thus, the temperature dependence of a phase transition (i.e., surface to air) can be expressed by the Clausius-Clapeyron equation when the system is at equilibrium. In environmental studies these plots have been generated from samples taken at different temperatures (even though a true equilibrium might not exist) and the slopes compared to literature slopes of the vapor pressure (Henry's constant, K_{oa} etc.).

The CC equation has been used by several researchers to explain the concentrations of various SVOCs (mainly PCBs and organochlorines) in the atmosphere (Hillery et al., 1997; Hoff et al., 1998; Simcik et al., 1999; Cortes et al., 1998). It has however, been found that the plots are often nonlinear and there is considerable scatter in some cases (Hoff et al., 1998, Cortes et al., 1999, Wania et al., 1998, Simcik et al., 1999). Some researchers (Wania et al., 1998; Hoff et al., 1998) have suggested that such behavior can be expected from the combination of exchange and transport processes that affect the air concentration at a remote site. Hoff et al. (1998) further suggest that the slopes of the CC plots (and hence the H values) can be interpreted in terms of relative importance of short- vs long-range transport. Their hypothesis is that lower slopes indicate that long-range transport controls atmospheric concentrations and that higher slope values (stronger temperature dependence) indicate that volatilization from local sources dominates atmospheric concentration. This means that the farther we move away from the source, the slopes become shallower (or temperature effect is less significant). Further, local exchange processes could control the atmospheric processes during the warmer months, and long-range transport processes could control the concentrations during the colder months. They support their conclusion by pointing out the fact that for North America it seems that there is a clear decline in slope with increasing distance from suspected PCB sources. However, it is now being suggested (Cortes et al., 1999) that for areas close to regions of current pesticide use, non-linearities and scatter in the CC plots may also result from pesticide usage.

Pesticides in air over the Peninsula

From the 2000 air data from Horn Point (data not shown), it is seen that most organochlorine pesticides (endosulfans, chlordanes etc.) are seen in the air throughout the year. Some compounds are more persistent than others. One way to ascertain the persistence of a compound in the atmosphere is to determine the half-life of the compound of interest. Half-lives can vary widely even for sites situated relatively close and can reflect the difference in the removal mechanisms. The atmospheric half-lives of the g-HCH have been found to range from 2.2 yr at Lake Michigan to 7.3 yr at Lake Ontario. The half-life of g-chlordane was 3.2 yr at Lake Michigan and that of trans-nonachlor was 9.2 yr at Lake Ontario (Cortes et al., 1998). Owing to the higher temperatures in the Delmarva Peninsula (as compared to the Great Lakes region), the half-lives of pesticides no longer in use (e.g. chlordanes) should be smaller than that observed in the Great Lakes region.

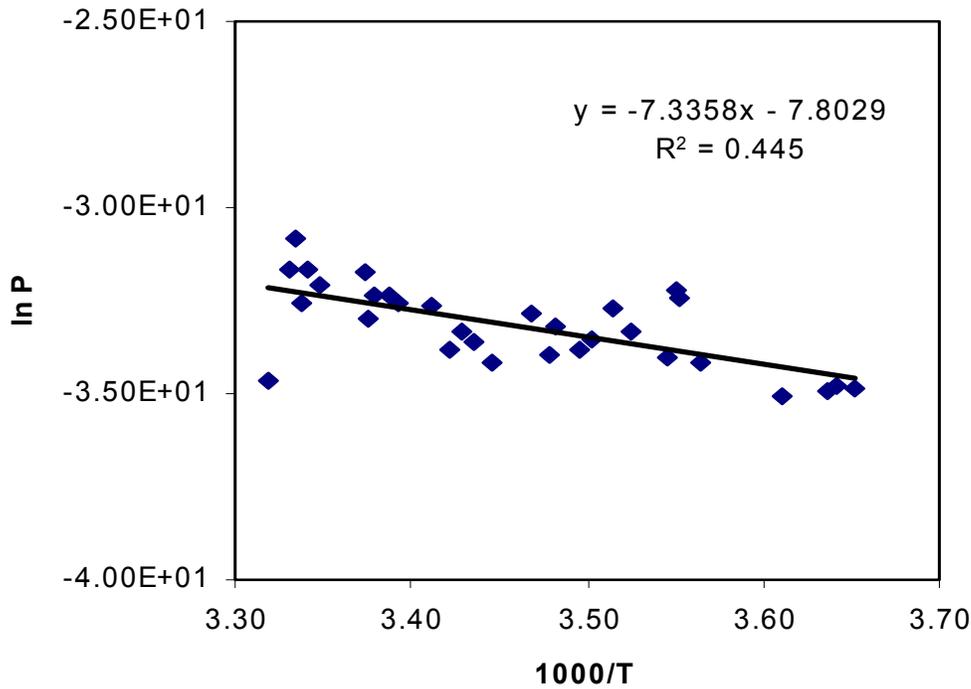


Figure 1. Clausius Clapeyron plot for a-endosulfan

For most pesticides currently in use (atrazine, endosulfans etc.) the concentrations peak during the application periods and are considerably lower during the rest of the year. The concentration pattern suggests that temperature is not the only factor governing the atmospheric concentrations. There is considerable non-linearity and scatter in the Clausius Clapeyron plot for a-endosulfan (Fig. 1) and temperature only explains about 40 % variation in the concentration. As has been suggested (Cortes et al., 1999) the atmospheric concentration for pesticides currently in use is highly dependent on the agricultural cycle.

We are currently determining the half-lives of the pesticides frequently detected in the air the Peninsula, taking into account the agricultural usage in the region. We use the equation suggested by Cortes et al. (1999):

$$\ln P = a_0 + a_1 \left(\frac{1}{T} \right) + a_2 t + \frac{a_3}{1 + \left(\frac{tMODa_4 - a_5}{a_6} \right)^2}$$

Where, 'a' symbols are constants, T is the temperature; t is the time when the sample was taken (in Julian days). The last term on the right is an expression for the agricultural cycle modeled as a Lorentzian (can also be Gaussian) function. The authors contend that the curvature in the CC plot can be attributed to agricultural usage. For pesticides no longer in use, the agricultural source term shall be removed and the equation reduces to (Cortes et al., 1998)

$$\ln P = a_0 + a_1 \left(\frac{1}{T} \right) + a_2 t$$

The half-life of the compound shall be ascertained from the value of the parameter a_2 . as

$$t_{1/2} = \frac{\ln 2}{a_2}$$

We are using the aerial concentration data from Horn Point site as it will the largest data set available. The pesticide concentrations available after initial analyses (ng/m^3) shall be converted to partial pressures using the ideal gas law. The parameters shall be determined using multiple linear regressions.

Determination of the atmospheric half-lives is the first step in quantifying the effect that agricultural usage has on atmospheric concentrations. Cortes et al. (1999) have reported that the estimated half-life for α -HCH went up by 50% when recent agricultural usage was accounted for. Incorrect half-lives jeopardize realistic risk assessment. For pesticides no longer in use, the half-lives help us in estimating the rate at which the concentrations are reducing. It is also possible that no plausible decrease for such compounds will be observed. This could point to the fact that the system is still not at equilibrium and the contaminated soils/water bodies are acting as sources of these compounds to the atmosphere. The correlation between aerial concentrations and usage is expected to be high. In the reverse case, that is, if the agricultural function does not greatly affect concentrations, other effects such as long-range transport from other areas might be examined.

Comparison of V/P partitioning of pesticides and PAHs

For the 2000 air data from Horn Point it is seen that the Junge-Pankow model under predicts the vapor particle partitioning of metolachlor and atrazine (Figure 2). It was seen that the model greatly under predicted the particle phase concentration in most cases. This is in contrast to the results of Bidleman et al. (1999) where they found that the model over predicted the distribution of organochlorines. There could be several reasons for the discrepancy. The fact that the deviations were more pronounced for the samples taken during the heavy agricultural activity, suggests that probably equilibrium was not reached. Sampling artifacts such as sorption of gaseous compounds onto the particles on the filter and onto the filter itself (Bidleman and Harner, 2000) could bias the results towards the particulate concentration. Such a possibility is being remedied by using two filters in subsequent sampling periods. Model limitations could also account for these observations (2001 onwards).

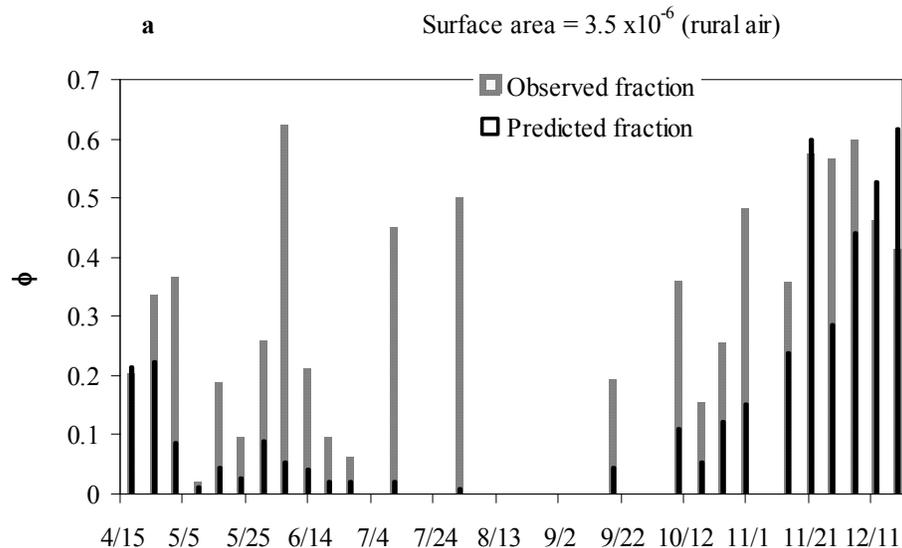


Figure 2. Vapor/Particle distribution of atrazine (Horn Point, 2000)

One of the major limitations of the model is that it fails to consider the humidity effects (Cotham and Bidleman, 1995), which might be quite significant in case of the modern polar pesticides: the greater the humidity, the greater would be the amount of water present on the particulates and consequently the greater would be the partitioning of the compound into the water phase on the particle. For PAHs, Pankow et al., (1993) found that PAH particulate fraction is inversely related to relative humidity, although the correlations were low. Delmarva Peninsula is a region with high relative humidity the year round. At the Horn Point site for April-September, 2000, the average relative humidity was 83.58% and the minimum value was 30.66%. Hence, a combination of compound properties and the climate might make humidity an important variable in predicting the V/P partitioning.

In a recent study, Arzayus et al., (2001) found that fractional concentrations of PAHs in the Chesapeake Bay sediment were positively correlated with their atmospheric dry deposition fluxes to the Bay. The authors concluded that atmospheric deposition of aerosol-bound PAHs to the watershed controls their influx to the Bay sediments. The fate of PAHs input to the Bay from gas deposition was determined to be uptake and metabolism within the aquatic food web rather than deposition to sediments. The results from this underline the importance of greater understanding of vapor/particle partitioning of PAHs.

For comparison, we have added PAH's to the toxic chemicals to be analyzed. The Delmarva Peninsula is largely agricultural; the industrial activity is limited at best. It is well established that the sources of PAHs in the environment are predominantly urban (Dachs et al., 2002, Simcik et al., 1997). Hence, it is reasonable to assume that, for most part, the PAH source to the Peninsula would be from the across the Bay (Washington and

Baltimore metropolitan areas) and from the west (the Atlantic ocean on the east largely rules out sources from that end). In contrast, the source of agricultural pesticides is local. The very location of the region sets it apart from the other studies, most of which have been conducted in urban areas with local sources of PAHs and distant pesticide sources. In the case of this study the region is rural with known sources of pesticides and distant PAH sources. The purpose is to compare the effectiveness of the Junge-Pankow model in predicting V/P partitioning of PAHs and pesticides in this region.

Significance

The data obtained as part of this project represents the largest data set available for pesticides in rain and air in the Delmarva Peninsula. The determination of atmospheric half-lives and effect of relative humidity on partitioning would help in better assessing the fate of these compounds in the environment as well as discriminate between regional and non-regional sources. While this project is near completion, another project (funded from CICEET) is underway with the addition of a third site. We plan to continue the analysis with the data from the 3-sites. We plan to use LandSat imagery to estimate. It is an indirect method of estimating emissions but is well suited in cases where sufficient pesticide usage data is not available. Estimates of amount of pesticides volatilized can be further used to determine the importance of runoff and aerial depositions in pesticide loadings to the Chesapeake Bay.

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